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ORIGINAL ARTICLE

Insect antifeedant potent 6-substituted ω-bromo-2-naphthones

G. Thirunarayanan *

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

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6-Substituted ω-bromo-2-naphthyl ketones;
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Abstract A series of some 6-substituted ω-bromo-2-naphthyl ketones have been synthesized by a greener synthetic method using fly-ash: water catalyzed aqueous phase reaction. The purities of these ketones and esters checked by their physical constants and spectral data have been published earlier in the literature. The insect antifeedant activities of these ketones have been studied using 4th instar larvae *Achoea janata* L and *castor semilooper*.

1. Introduction

Alkyl and aryl carbonyl derivatives possess multipronged biological activities such as antimicrobial, antiviral, antifertile, antiplosmodial and antioxidants (Reddy et al., 2010; Thirunarayanan et al., 2011a,b; Arulkumaran et al., 2010; Thirunarayanan and Vanangamudi, 2011). Presence of polar, carbonyl, and alkene groups in aromatic rings are origin for these multipronged biological activities. Halogenated enol and enone including chalcones show insect antifeedant activities (Thirunarayanan, 2008; Thirunarayanan et al., 2010; Nalwar et al., 2009). Acyl and halogenated acyl derivatives possess multipronged biological activities and are used in agricultural and medicinal fields. Stereospecific and stereo selective bio-active acyl halo derivatives have been synthesized using the green halogenation reaction (Kajigaeshi and Kakinami, 1995; Bora et al., 2001), esterification (Zhao et al., 2008) and complex reactions like callixrane (Chen and Munot, 2005) formation. Solvent free organic reactions were applied for the synthesis of carbonyl compounds due to operational simplicity, easy work-up, better yield and eco-friendly nature (Lou and Xu, 2002; Cave et al., 2001; Kalluraya and Ray, 2003; Thirunarayanan and Vanangamudi, 2006; Thirunarayanan et al., 2010, 2011; Bamoharram et al., 2007; Adimurthy et al., 2006). Among these reactions bromination is useful for the formation of carbon–bromine bonds in many kinds of carbonyl compounds (Moumne et al., 2006; Paul et al., 1996). Many catalysts, reagents and metal salts like copper(II) bromide (King and Ostrum, 1964), *N*,*N*-dimethylformamide (Levene, 1943; Pearson et al., 1973), 1,4-dioxanebromooxoniumbromide (Paul et al., 2003), *N*-bromosaccharin (Sanches and Fumarola, 1982), human eosinophils (Curran, 1989), acid chlorides (Cajetan et al., 2006) and pyridiniumbromochromate (Patwari et al., 2003) are employed for the bromination of alkyl as well as aryl compounds. Fly-ash, activated fly-ash, fly-ash:H_2O are also used as catalysts for the synthesis of organic compounds. Fly-ash contains various chemical species such as (Thirunarayanan, 2010;

* Tel.: +91 4144220015.
E-mail address: drgtnarayanan@gmail.com.

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Gopalakrishnan et al., 2005, 2006), SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO and insoluble residues in fly-ash. These species involve the promoting effect of carbon–carbon bond formation or halogenation of methyl group in the side chain during the course of reaction. In the present work the author has taken efforts to brominate 6-substituted 2-naphthyl ketones with brominating reagents like Winkler solution (bromate–bromide solution) and aqueous phase catalyst fly-ash under solvent free conditions and studied the insect antifeedant activities of synthesized acyl bromides.

2. Experimental

2.1. Materials and methods

Fly-ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli, Tamilnadu, India. All chemicals used were purchased from Sigma–Aldrich and E-Merck Chemical Company. Melting points of all ω-bromo ketones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Further the purities of these ω-bromo ketones were checked by their spectral data published earlier in the literature. Electron impact (EI) (70 eV) and chemical ionization mode FAB^+ mass spectra were recorded with a VARIAN 500 spectrometer.

2.2. General procedure for the bromination of 6-substituted 2-naphthyl methyl ketones (Thirunarayanan et al., 2011b)

In a 100 ml flask, 6-substituted 2-naphthyl methyl ketones (4.16 mmol) in aqueous ethanol (20 ml), 1.5 g of fly-ash and 10 ml of water were taken. To this mixture Winkler's solution (bromate–bromide solution) 10 ml was added drop wise with stirring for 45 min until a decoloration of orange solution took place (Scheme 1). The completion of reaction was monitored by TLC. After completion of the reaction the ω-brominated products were separated by column chromatogram using ethyl acetate–dichloromethane (6:4) that gave the pale yellow products of ω-bromo-6 substituted acetonaphthones, in more than 70% yield. Further usage of this catalyst is found to be ineffective. In this protocol the reaction gave good yields of the brominated products, during α-bromination (substitution) without any environmental discharge. The analytical and spectral data of all synthesized ω-bromo-6 substituted 2-naphthyl ketones are presented in Table 1.

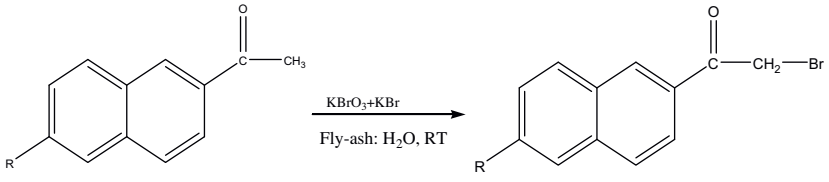
3. Results and discussion

The multipronged activities present in different ω-bromo-2-naphthyl ketones are intended to examine their insect antifeedant activities against castor *semilooper*. The larvae of *Achoea janata* L were reared as described on the leaves of castor *Riclmus cammunls* in the laboratory at the temperature range of 26 °C ± 1 °C and a relative humidity of 75–85%. The leaf-disc bioassay method (Thirunarayanan, 2008, 2010) was used against the 4th instar larvae to measure the antifeedant activity. The 4th instar larvae were selected for testing because the larvae at this stage feed very voraciously.

3.1. Measurement of insect antifeedant activity ω-bromo-6 substituted naphthones

Leaf discs of a diameter of 1.85 cm were punched from castor leaves with the petioles intact. All acyl ketones were dissolved in acetone at a concentration of 200 ppm dipped for 5 min. The leaf discs were air-dried and placed in 1 l beaker containing little water in order to facilitate the translocation of water. Therefore the leaf discs remain fresh throughout the duration of the rest, 4th instar larvae of the test insect, which had been preserved on the leaf discs of all ω-bromo-6 substituted naphthones and allowed to feed on them for 24 h. The area of the leaf disc consumes were measured by Dethlers (Dethler, 1947; Thirunarayanan et al., 2010) method. The observed antifeedant activity of ω-bromo-6 substituted naphthones are presented in Table 2.

The results of the antifeedant activity of ω-bromo-6 substituted naphthones presented in Table 2 reveal that the compounds **3–6** were found to reflect remarkable antifeedant activity among all other naphthones. This test is performed with the insects which are only two-leaf disc soaked under the solution of this compound. Compounds **4–6** also show enough antifeedant activity but lesser than **6**. Further compound **4** was subjected to measure the antifeedant activity at different 50, 100, 150 ppm concentrations and the observation reveals that as the concentrations decreased, the activity also decreased. It is observed from the results in Table 3 and that



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No	1	2	3	4	5	6	7	8	9
R	H	F	Cl	Br	OH	OCH_3	CH_3	SCH_3	SO_2CH_3

Scheme 1 Synthesis of ω-bromo-6 substituted acetonaphthones.

Table 1 Analytical data and physical constants of 6-R-ω-bromo-2-acetonaphthones.

Entry	R	Molecular formula	Molecular weight	M.p. (°C)	Yield (%)	Mass fragments (*m*/*z*)
1	H	$C_{12}H_9BrO$	248	81–82 (80)[a]	75	248(45%)[M^+], 250(72%)[M^{+2}], 169(37%), 155(100%), 151(67%), 127(54%), 121(64%), 107(76%), 93(63%), 91(58%), 72(73%), 43(76%), 28(43%), 14(49%)
2	F	$C_{12}H_8BrFO$	266	85–86 (84–85)[a]	78	266(65%)[M^+], 268(63%)[M^+2], 270(71%)[M^{+4}], 2476(35%), 187(45%), 173(100%), 145(76%), 107(65%), 95(56%), 77(54%), 14(52%)
3	Cl	$C_{12}H_8BrClO$	282	137–138 (137–138)[a]	75	282(39%)[M^+], 284(53%)[M^{+2}], 286(57%)[M^{+4}], 207(42%), 193(100%), 165(87%), 141(67%), 107(67%), 79(32%), 77(54%)
4	Br	$C_{12}H_8Br_2O$	326	113–114 (112–113)[a]	72	326(45%)[M^+], 328(56%)[M^{+2}], 330(87%)[M^{+4}], 247(82%), 233(100%), 205(76%), 153(43%), 107(72%), 91(36%), 77(62%)
5	OH	$C_{12}H_9BrO_2$	264	98–99 (97–98)[a]	74	264(56%)[M^+], 266(63%)[M^{+2}], 185(78%), 171(100%), 153(35%), 107(47%), 105(53%), 91(45%), 77(68%), 52(23%), 28(46%)
6	OCH_3	$C_{13}H_{11}BrO_2$	278	131–132 (131–132)[a]	77	278(42%)[M^+], 280(61%)[M^{+2}], 279(43%), 247(48%), 199(58%), 185(100%), 157(72%), 118(37%), 107(67%), 91(61%), 77(34%), 40(37%), 28(14%), 15(34%)
7	CH_3	$C_{13}H_{11}BrO$	262	108–109 (107–108)[a]	75	262(46%)[M^+], 268(63%)[M^{+2}], 247(56%), 183(84%), 169(100%), 141(68%), 126(68%), 107(63%), 91(73%), 77(62%), 15(14%)
8	S–CH_3	$C_{13}H_{11}BrOS$	294	135–136 (134–135)[a]	73	294(34%)[M^+], 296(46%)[M^{+2}], 297(56%)[M^{+3}], 247(34%), 215(100%), 201(67%), 173(43%), 147(75%), 132(67%), 107(81%), 100(54%), 91(34%), 32(34%)
9 78	SO_2–CH_3			$C_{13}H_{11}BrO_3S$ 326 116–117 (116–117)[a]		326(45%)[M^+], 327(65%)[M^{+1}], 328(73%)[M^{+2}], 311(43%), 247(100%), 233(30%), 205(48%), 107(72%), 91(36%), 77(62%), 53(43%), 28(33%), 15(54%)

[a] Thirunarayanan et al. (2011b).

Table 2 Insect antifeedant activities of ω-bromo 6-substituted acetonaphthones.

Entry	R	4–6 pm	6–8 pm	8–10 pm	10–12 pm	12–6 am	6–8 am	8 am–12 Nn	12Nn–2 pm	2–4 pm	Total leaf disc consumed in 24 h
1	H	0.05	0.5	0.5	0.5	0.5	1	1	1	1	6.5
2	F	0.5	0.25	0.25	0.5	0.5	0.5	1	1	0.5	5
3	Cl	0.25	0.25	0.25	0.25	0.5	0.5	1	1	0.5	4.5
4	Br	0.25	0.5	0.25	1	0.5	0.25	0.25	0.25	0.25	3.5
5	OH	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	4
6	OCH_3	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	4
7	CH_3	1	2	2	1	0	0	1	1	1	9
8	S–CH_3	1	1	0.5	0.5	0.5	1	1	1	1	8
9	SO_2–CH_3	1	0.5	0.5	1	1	0	1	1	1	9

Number of leaf discs consumed by the insect (values are mean + SE of five).

Table 3 Antifeedant activity of compound ω-bromo-6-bromo-2-acetonaphthone **(4)** at 3 different concentrations.

ppm	4–6 pm	6–8 pm	8–10 pm	10–12 pm	12 am–6 am	6–8 am	8 am–12 Nn	12 Nn–2 pm	2–4 pm	Total leaf disc consumed in 24 h
50	0.5	0.25	0.25	0	0	0	0	0	0	1
100	0	0.25	0.25	0	0	0	0	0	0	0.05
150	0.25	0.5	0.25	0	0.25	0	0	0	0	1.25

Number of leaf discs consumed by the insect (values are mean + SE of five).

the ω-bromo-6 substituted naphthone **4** showed an appreciable antifeedant activity at 100 ppm concentration.

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